

# Charged colloids at low ionic strength: macro- or microphase separation?

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Phase separation in charged systems may involve the replacement of critical points by microphase separated states, or charge-density-wave states. A density functional theory for highly charged colloids at low ionic strength is developed to examine this possibility. It is found that the lower critical solution point is most susceptible to microphase separation. Moreover the tendency can be quantified, and related to the importance of small ion entropy in suppressing phase separation at low added salt. The theory also gives insights into the colloid structure factor in these systems.

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There has been much interest recently in statistical physics in charged soft matter systems. Whilst much of this is biologically inspired (eg DNA condensation [1]), there has also been a long standing controversy in the colloid science community over the anomalous behaviour of charge stabilised colloidal suspensions at low ionic strengths [2]. Recently [3,4], it has been suggested that the anomalies in these systems may be understood in terms of a miscibility gap which is the analogue of the vapour-liquid coexistence in the restricted primitive model (RPM) of 1:1 electrolytes [5]. Arguably a theoretical consensus is emerging, although there remain a number of competing theories [6].

In all these examples, the crucial role of the counterions should not be underestimated. For the case of charged colloidal suspensions, for example, the theories show that the overall phase stability is almost entirely due to the entropy of the counterions [3,4]. The same effect can be said to underpin the solubility of many water-soluble polymers [7]. The basic point is that bulk phase separation in a charged system must be into electrically neutral phases. If this involves significant fractionation of counterions, an entropic penalty will be incurred which tends to suppress phase separation.

Clearly though, if bulk phase separation is suppressed, a possibility still exists to undergo *microphase separation*, where electroneutrality can be broken locally. Critical points are particularly susceptible to this, as first shown by Nabutovskii, Nemov and Peisakhovich (NNP) using a Landau-Ginzburg theory [8]. Consider density fluctuations at wavevector  $q$ . At  $q \rightarrow 0$ , fluctuations are restricted to electrically neutral combinations, but for  $q > 0$  fluctuations can violate electroneutrality increasingly easily. Thus one might expect some softening of the modes. Indeed, if the only terms to  $O(q^2)$  come from the long range Coulomb law, the analysis below implies that all partial structure factors have a *minimum* at  $q = 0$ . Since the  $q = 0$  partial structure factors diverge as one approaches a critical point, this suggests there must exist regions around critical points where a divergence at  $q > 0$  occurs first, indicative that the critical behaviour is preempted by microphase separation. However, there

are often other terms arising at  $O(q^2)$  from elsewhere which destroy the phenomenon. A closely analogous microphase separation for polyelectrolytes in poor solvents has also been examined [9], but in the present study microphase separation is driven purely by electrostatic effects.

Let us start by constructing a simplified but physically motivated model for the anomalous behaviour in charged colloidal suspensions. Consider the macroions as spheres of charge  $Z$ , diameter  $2a$ , and number density  $\rho_M$  (volume fraction  $\phi = 4\pi a^3 \rho_M / 3$ ). There are small counterions and coions at number densities  $\rho_-$  and  $\rho_+$  respectively. The solvent is a dielectric continuum. Without loss of generality, I suppose the small ions are univalent, and there is only one species of counterion [10]. Since the coions come from added salt, it will be convenient to write  $\rho_+ = \rho_S$ . Overall, the system is electrically neutral and  $\rho_- = \rho_S + Z\rho_M$ , but  $\delta\rho_{\pm}$  will be retained for fluctuations.

Each macroion polarises the surrounding electrolyte solution, and becomes surrounded by a ‘double layer’. It has been shown by many workers [3,11,12] that the self energy of the macroion with its double layer, in Debye-Hückel theory, is  $(Z^2 l_B kT / 2a) \times h(\kappa a)$ . In this  $l_B = e^2 / \epsilon kT$  is the Bjerrum length, the function  $h(x) = 1/(1+x)$  [13], and the Debye screening length,  $\kappa^{-1}$ , is given by  $\kappa^2 = 8\pi l_B \rho_I$  where  $2\rho_I = \rho_- + \rho_+ = Z\rho_M + 2\rho_S$  is (twice) the ionic strength. This energy has a well known interpretation: it corresponds exactly to a *spherical capacitor*, charged  $\pm Ze$ , with one plate at the macroion surface and the second a distance  $\kappa^{-1}$  away [14].

The simplest model free energy based on this is

$$F/VkT = \rho_S \log \rho_S + (\rho_S + Z\rho_M) \log(\rho_S + Z\rho_M) + \rho_M \log \rho_M + \rho_M (Z^2 l_B / 2a) h(\kappa a). \quad (1)$$

The first three terms are the ideal terms, and the last is the self energy of macroions at number density  $\rho_M$ . The most important omission from this is the contribution from the macroion-macroion interactions. Whilst this plays a significant role in structuring the macroions, it has been demonstrated elsewhere [4] that it is *less significant* than the self energy, as regards the appearance of

a miscibility gap. Moreover, by leaving this contribution out of the theory, we will see quite clearly how structure can develop in the system in the absence of pair interactions.

A typical phase diagram corresponding to the above free energy is shown in Fig. 1, for  $Z = 10^3$  and  $2a = 100$  nm. It comprises a simple miscibility gap, limited above and below by critical solution points as the salt concentration is varied. The gap occurs at very low ionic strengths, and only appears if the charge on the macroions is sufficiently high ( $Zl_B/a \gtrsim 13.4$  for  $2a$  in the range 10–1000 nm).

Now, the NNP scenario could occur at either critical point. To examine this therefore, I construct a density functional theory to correspond to the free energy introduced above. The ideal terms become  $kT \int d^3\mathbf{r} \rho_i(\mathbf{r}) \log \rho_i(\mathbf{r})$  ( $i = +, -, M$ ), and I introduce the *ansatz* that the self energy generalises in the obvious way to  $\int d^3\mathbf{r} \rho_M(\mathbf{r}) f_N^{\text{self}}(\mathbf{r})$  where  $f_N^{\text{self}} = (Z^2 l_B kT / 2a) h(\kappa a)$  is the self energy per particle evaluated using the local ionic strength at the particle centre,  $\kappa^2 = 8\pi l_B \rho_I(\mathbf{r})$ . Finally, an electrostatic contribution has to be added:  $l_B kT \int d^3\mathbf{r} d^3\mathbf{r}' \rho_Z(\mathbf{r}) \rho_Z(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ , where  $\rho_Z(\mathbf{r}) = Z\rho_M(\mathbf{r}) + \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$  is the local charge density.

To examine the stability of the system against microphase separation, expand the above density functional about the homogeneous state to quadratic order. For fluctuations at a wavevector  $q$  this results in

$$\begin{aligned} \frac{\delta F}{VkT} = & \frac{|\delta\rho_+|^2}{2\rho_S} + \frac{|\delta\rho_-|^2}{2(\rho_S + Z\rho_M)} + \frac{|\delta\rho_M|^2}{2\rho_M} \\ & + \frac{2\pi l_B}{q^2} |Z\delta\rho_M + \delta\rho_+ - \delta\rho_-|^2 \\ & + \frac{Z^2 l_B}{2a} \left[ 8\pi^2 l_B^2 a^4 \rho_M h_1(\kappa a) |\delta\rho_I|^2 \right. \\ & \left. - 2\pi l_B a^2 h_2(\kappa a) (\delta\rho_M \delta\rho_I^* + \delta\rho_M^* \delta\rho_I) \right] \end{aligned} \quad (2)$$

The functions are  $h_1(x) = (1 + 3x)/(x^3(1 + x)^3)$  and  $h_2(x) = 1/(x(1 + x)^2)$ . From this the macroion structure factor  $S(q) = \langle |\delta\rho_M(q)|^2 \rangle$  is extracted in the standard way [15]. The behaviour of  $S(q)$  is examined as a function of  $\phi$  and  $\rho_S$ , looking for the unstable regions in the  $(\phi, \rho_S)$ -plane where  $1/S(q) < 0$ .

At  $q = 0$  the spinodal instability region corresponding to the free energy in Eq. (1) is recovered. For  $q > 0$  the region of instability *always expands*. This is because the  $q$ -dependence arises solely from the long range electrostatic term, thus, as alluded to above,  $S(q)$  always has a minimum at  $q = 0$ . But a clear difficulty emerges when the behaviour for large  $q$  is examined, since the instability region expands to fill the entire plane; there is no effective penalty against microphase separation at vanishingly small wavelengths.

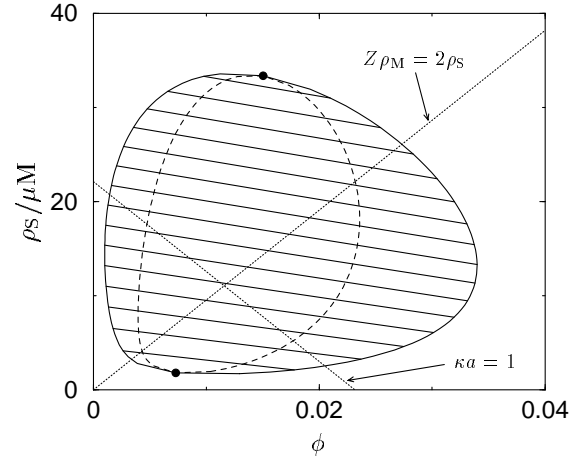


FIG. 1. Miscibility gap at low ionic strength for model free energy, Eq. (1) in text, at  $Z = 10^3$  and  $2a = 100$  nm. Also marked are the lines where the counterions and added salt contribute equally to the ionic strength ( $Z\rho_M = 2\rho_S$ ), and where the macroion self energy function varies most rapidly ( $x = \kappa a = 1$ ).

In fact the *ansatz* for the self energy term has omitted an obvious but crucial effect, namely one would not expect a macroion to be sensitive to variations in the local ionic strength over distances much smaller than its size. Motivated by weighted local density theories for liquids [16], I therefore introduce an additional *smoothing ansatz*. It turns out that the precise form does not matter greatly, for instance one can replace the local ionic strength by  $\bar{\rho}_I(\mathbf{r}) = \int d^3\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|) \rho_I(\mathbf{r}')$  where  $w(r)$  is a smoothing kernel of range  $a$  [17], but equally one might smooth  $\kappa$  or  $f_N^{\text{self}}$ . All forms result in the appearance of extra multiplicative factors,  $w_1(qa)$  and  $w_2(qa)$ , in the last two terms of Eq. (2). The  $w_i(qa)$  are related to the Fourier transform of  $w(r)$ , and satisfy  $w_i \rightarrow 1$  at  $q \rightarrow 0$ ,  $w_i \rightarrow 0$  at  $q \rightarrow \infty$ . (More generally I expect  $h_i(\kappa a, qa)$  such that  $h_i \rightarrow 0$  for  $qa \rightarrow \infty$ .) With this *ansatz*, progress can be made without developing a detailed theory by investigating various possibilities for  $w_i$ . The results reported below have been carried out assuming  $w_1 = w_2 = \exp(-\alpha q^2 a^2)$  with  $\alpha$  a numerical prefactor of order unity. Very similar results are obtained for  $w_i = 1/(1 + \alpha q^2 a^2)$ .

Typical results from this modified theory are shown in Figs. 2 and 3, for  $\alpha = 1$ . In Fig. 2, the spinodal instability at  $q = 0$  is recovered as before. For  $q > 0$ , the instability region is again expanded in the vicinity of the lower critical point, but is now *reduced* in the vicinity of the upper critical point. For  $qa \gg 1$  the instability disappears completely, since the self energy which drives the instability is now insensitive to short wavelength fluctuations. Below the lower critical point, therefore, there is a region (delimited by the heavy dashed line in Fig. 2) where  $S(q)$  diverges at some  $q^* > 0$ , corresponding to the appearance of microphases.

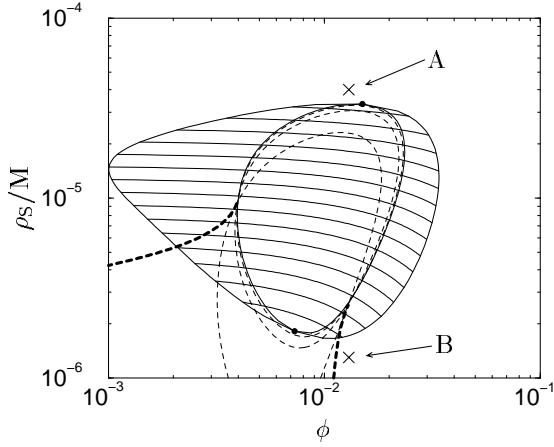


FIG. 2. Phase diagram in double logarithmic plot, showing as dashed lines the contours of divergence of  $S(q)$ , from  $q = 0$  (identical to original spinodal), through  $qa = 0.05, 0.1, 0.2$  (light dashed lines) to  $q = q^*$  (heavy dashed line) where the maximum in  $S(q)$  diverges (typically  $q^*a \lesssim 0.5$ ). The structure factors corresponding to the marked points are given in Fig. 3.

These results are reflected in the macroion structure factors, two examples of which are shown in Fig. 3. Near the upper critical point the structure factor turns up to a maximum as  $q \rightarrow 0$ , developing a divergence at  $q = 0$  as the (mean field) critical point is approached. Near the lower critical point a peak appears in  $S(q)$  at  $q^* > 0$ . The peak diverges as one approaches the boundary of the microphase instability region. Note that the appearance of a peak in the macroion structure factor  $S(q)$  is unusual because there are no direct macroion interactions in the theory as constituted above. This shows how structure can arise in a charged system independent of the existence of (effective) pair interactions.

To relate the results to possible experiments, one should of course investigate the significant contribution to the structure factor from the omitted macroion interactions. Elsewhere it is argued that, at these low ionic strengths, the macroions are effectively a one-component plasma (OCP) in the strong coupling limit [4], whose structure factor resembles that of hard sphere (HS) fluid close to the freezing transition [18]. A rescaled  $S(q)$  for HS at freezing is compared with the present calculations in the inset in Fig. 3. The additional structure arising from the self energy theory above appears to lie well within the first peak, and moreover the amplitudes match quite closely. Thus the appearance of a maximum at  $q = 0$  or a peak at very low  $q$  may well be experimentally observable. This may be the explanation of the anomalously large  $S(q \rightarrow 0)$  reported recently for colloidal suspensions at low ionic strengths [19].

Let us turn to the effect of  $\alpha$ . Recall that  $\alpha$  is a measure of the degree of smoothing: the range of the smoothing kernel is  $\sim a\sqrt{\alpha}$ . All the results discussed above were at  $\alpha = 1$ . If  $\alpha \lesssim 0.338$ , microphases ap-

pear at the *upper* critical point too. On the other hand, if  $\alpha \gtrsim 1.961$  microphase separation at the lower critical point disappears. One would expect increasing  $\alpha$  to suppress microphase separation, since greater smoothing is bound to reduce  $q^*$ , but the difference between the two critical points is suggestive. These critical values of  $\alpha$  are more general than the assumed form of  $w_i(q)$ , since they only depend on the  $q^2$  coefficient in the expansion  $w_i(q) = 1 - \alpha q^2 a^2 + O(q^4)$  [20]. They are a measure of the susceptibility of the critical point to replacement by microphases (if  $\alpha$  could be treated as a control variable, the critical values would correspond to Lifshitz points in the phase diagram).

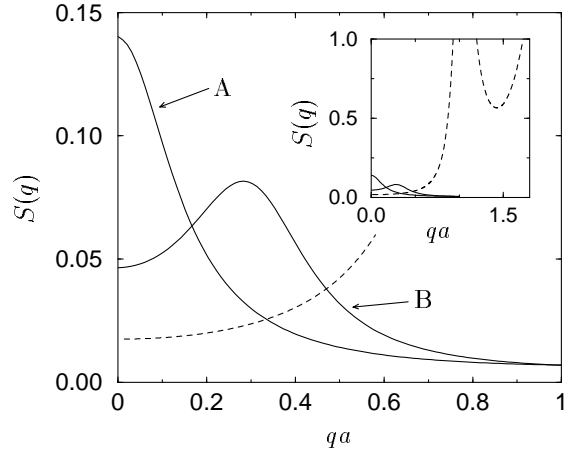


FIG. 3. Structure factor in vicinity of miscibility gap. The state points are those marked in Fig. 2. The dashed line is the structure factor expected from the interparticle repulsions at a scaled volume fraction around freezing (all normalised such that  $S(q) \rightarrow 1$  at  $q \rightarrow \infty$ ).

This calculation sheds light on the reason for a *closed loop* miscibility gap. As  $\rho_S$  is increased, an upper critical point is expected since the self energy ceases to be strongly state point dependent for  $\kappa a \gg 1$  or  $\rho_S \gg Z\rho_M$ , where it simply shifts the macroion chemical potential (see lines in Fig. 1). As  $\rho_S \rightarrow 0$  though, it is perhaps unexpected to encounter a *second* critical point. Its appearance appears to be connected to the small ion entropy effect discussed in the introduction. The evidence for this is twofold. Firstly, as already commented upon, the lower critical point is more susceptible to microphase separation. This is in accord with the idea that phase separation is suppressed by small ion entropy, since in microphase separation, the system gains entropy by distributing the small ions more uniformly than would be allowed if strict electroneutrality had to be satisfied at each point.

The second piece of evidence concerns the rate at which the *Donnan potential difference*  $\Delta\bar{\psi}$  vanishes as one approaches the critical point. Recall that  $\Delta\bar{\psi}$  arises be-

cause the interface can acquire a dipole moment density (per unit area). In the present system, a dipole moment density appears to arise because the jump in small ion densities is spread out more broadly than the jump in macroion densities (although this remains to be confirmed with a detailed calculation [21]). Remarkably, one can calculate  $\Delta\bar{\psi}$  without detailed knowledge of the structure of the interface [4]. I find that  $\Delta\bar{\psi}$  vanishes as  $\Delta\phi/\phi_{\text{crit}}$  as the critical points are approached, with a constant of proportionality  $\approx 8.00$  for the upper critical solution point, and  $\approx 16.9$  for the lower one. This again indicates the growing importance of small ion entropy (broadening the jump in small ion densities) as the lower critical point is approached.

Note that  $\Delta\bar{\psi}$  is an order parameter which strictly vanishes in symmetric models such as the RPM. Apart from general remarks by Nabutovskii and Némov [22], the critical behaviour of asymmetric primitive models seems to have received much less attention than the RPM [5], and there may be interesting effects connected to a non-vanishing  $\Delta\bar{\psi}$ .

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far as Debye-Hückel theory is applicable.

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[17] Note that in the phase separation region there is only one significant length scale since  $\kappa^{-1} \sim a$ .  
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